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(54) Title: ELECTROCHEMICAL ENERGY STORAGE AND POWER DELIVERY PROCESS UTILIZING IRON-SULFUR COUPLE

(57) Abstract

An electrochemical process for energy storage and power generation comprises a single cell or an array of unit cells (10), each cell comprising a $+^{ve}$ electrode (12) and a $-^{ve}$ electrode (14) with a membrane in each cell dividing it into $+^{ve}$ and $-^{ve}$ chambers (22C and 24C) for posilyte and anolyte solutions (22, 24) which are recirculated through separate pumps (26, 28) and storage tanks (32, 34) and back to the chambers. An iron-sulfur couple is employed, the overall reaction being: $2Fe^{3+} + S^{2-} = 2Fe^{2+} + S$(Eq.8), the Fe^{3+} ions being provided as the chloride, bromide or iodide and the sulfide being provided as the sodium, potassium, lithium or ammonium salts. The $+^{ve}$ chamber contains a soluble ionic salt which acts as a charge carrier during energy storage, preferably sodium or potassium chloride. Means are provided to offset pH in the system, and further means are provided for a third chamber (23C) whereby the system is more effectively electrically rechargeable.

ELECTROCHEMICAL ENERGY STORAGE AND POWER DELIVERY
PROCESS UTILIZING IRON-SULFUR COUPLE

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The present invention relates generally to energy storage and power generation systems wherein compensating electrochemical reactions occur at opposite positive (hereinafter $+^{ve}$) and negative (hereinafter $-^{ve}$) electrodes and energy is stored in, and drawn from, an electrolyte in charge and discharge cycles. The reactions in the class of such systems of interest for the purposes of this invention are substantially reversible such that driving current into such a system charges the system by storing energy in chemical reactants. Chemical reactions take place on either side of an ion transport system (such as a membrane or multiple membranes and/or intermediate cell sections) with selective charge carriers being transported through the membrane. During power generation these chemical reactions reverse supplying current (power) to a load.

Some systems reconstitute or regenerate the reagents to restore the cell, as compared to driving current into the cell.

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Such energy systems have been known for many years. Major limitations of these systems have resulted from the practical application of what seems to be a simple direct chemical process. Hazardous materials, efficiencies, system size, plugging and clogging, gas formation, "plating out" or precipitation of the materials, membrane diffusion limitations, cost of materials and cost of operation highlight the practical problems. Another limitation of such systems is the loss of power output as the system discharges.

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The fundamental chemical process in these systems

is characterized by a chemical equation where the action proceeds in one direction in the charging of the system and in the opposite direction during the power generation by the system. An example of a redox system is given by the following chemical equation, the term "redox" defining reactions in which a reduction and a complementary oxidation occur together.

$$\text{Eq. 1} \qquad Cr^{2+} + Fe^{3+} \rightarrow Cr^{3+} + Fe^{2+}$$

In this system, limitations exist since the chromium is expensive and the chromium and iron, meant to be on either side of a membrane, cross over contaminating the other side. This necessitates frequent reprocessing of the electrolyte. Furthermore, noble metal catalysts are required to promote the reaction. Also, the system pH must be controlled to prevent gas formation.

US-A-3920474 discloses a fuel cell which uses a source of sulfide ions as fuel in the negative chamber of a cell in which the positive and negative chambers are separated by an ion-transfer or mechanically porous membrane. The catholyte may comprise ferric chloride with the overall reaction being

$$2Fe^{3+} + S^{2-} \rightarrow S + 2Fe^{2+}$$
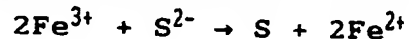
This system acts as a fuel cell only for the delivery of power to a load and cannot be electrically recharged.,

US-A-4485154 discloses an electrically rechargeable anionically active energy storage and power delivery system using a sulfide-polysulfide anolyte reaction and an iodide-polyiodide, chloride-chlorine or bromide-bromine catholyte reaction.

An object of this invention is to provide a redox

process for energy storage and power delivery process where no solids are deposited on the electrodes and where the electrolytes can be electrically restored at least initially.

5   It is yet another object of the invention to provide a safe process with a sufficient power density depending upon the application needs.

Another object of this invention is to provide substantially full power even at low states of charge

10   of the system, i.e. the system power production stays constant over time maintaining substantially the same output until close to complete discharge.

The foregoing objects are met in a process which utilizes a chemical reaction characterized by the

15   following overall chemical equation,

$$\underline{Eq.\ 2} \qquad\qquad 2Fe^{3+} + S^{2-} \rightarrow 2Fe^{2+} + S$$
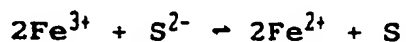
where the ions are provided from salts of these

20   reagents, preferably iron chloride in aqueous solution on the $+^{ve}$ side and potassium sulfide solution on the $-^{ve}$ side. It will be understood that other iron salts may also be used, such as the bromide or iodide. Whilst K_2S is preferred for use in the invention,

25   sodium sulfide, Na_2S, will work almost as well, except that Na_2S is much less soluble than K_2S.

The process of the present invention is carried out in a single cell or in an array of cells, each of which has a $+^{ve}$ electrode and a $-^{ve}$ electrode, in which

30   circulating electrolyte flows are maintained. An ion exchange membrane between the electrodes divides the cells into $+^{ve}$ and $-^{ve}$ chambers. The electrolyte circulating through the $-^{ve}$ chamber during power delivery contains sulfide ions and the electrolyte

35   circulating through the $+^{ve}$ chamber during power

delivery contains Fe^{3+} ions. Additionally a soluble,
ionic salt selected from sodium, potassium, lithium
and ammonium salts, circulates through the $+^{ve}$ chamber
of the cell during energy storage (charging) and acts
as a charge carrier. For some purposes, as described
below in further detail, a double membrane is provided
forming a buffer chamber between the membranes.

The electrochemical reaction of Eq. 2 actually
occurs in separate but dependent iron and sulfur
reactions. The iron reaction takes place on the $+^{ve}$
side of the membrane and the sulfur reaction on the $-^{ve}$
side. The charge balance is provided by the transport
of sodium, potassium, lithium or ammonium ions across
the membrane.

When charging occurs, Eq. 2 goes from right to
left, and when discharging (power supplied to a load),
Eq. 2 goes from left to right.

The reagents involved in the process are as
follows:
In the discharged state:
the $+^{ve}$ side contains $FeCl_2$ + KCl + H_2O, and
the $-^{ve}$ side K_2S_5 + H_2O.
In the charged state:
the $+^{ve}$ side $FeCl_3$ + H_2O + KCl, and
the $-^{ve}$ side K_2S + H_2O.

The stoichiometric ratio of $FeCl_3$ and K_2S required
to fully utilize these reagents is 4 moles $FeCl_3$ to
2.5 moles K_2S, according to the equation:

Eq. 2A $8\ FeCl_3 + 5\ K_2S \rightleftharpoons 8\ FeCl_2 + K_2S_5 +$
8 KCl
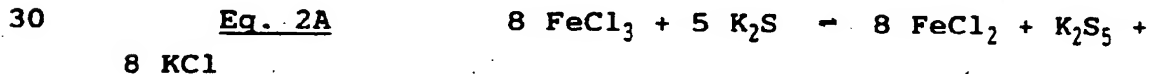
The primary charge carriers are potassium ions,
K^+, which are readily transported through the ion
exchange membrane. The Fe^{3+} or Fe^{2+} are poorly

transported through the membrane despite the fact that
it is a cation exchange membrane. The sulfide ions,
S^{2-}, are anions that are not transported through the
cation exchange membrane.

5   These transport properties are most important.
Iron sulfide is insoluble in water. Hence, any
transport of either sulfide across from the $-^{ve}$ side to
the $+^{ve}$ side, or the transport of ferric or ferrous
from the $+^{ve}$ side to the $-^{ve}$ side will result in
10   unwanted precipitates which will clog the membrane.

        In addition to the above, another feature working
in favour of the system of this invention is that
during discharge the transport or charge carrier
processes are going in the correct direction. That
15   is, all positive ions are trying to move into the $+^{ve}$
side, and all $-^{ve}$ ions are attempting to move into the
$-^{ve}$ side. Since the membrane is a cation exchange
membrane, very few Cl^- ions are lost to the $-^{ve}$ side.

        During charge, however, the opposite is true, and
20   a cell with only two compartments will not accept a
charge if charge carrying ions are not present in the
$+^{ve}$ chamber. Attempting to charge such a cell results
in an immediate high resistance and virtually no
current flows. Substantially no iron ions are
25   transported across the membrane, and because the
membrane is a cation exchange membrane, substantially
no S^{2-} ions are transported across it. In fact, any S^{2-}
attempting to migrate through the membrane reacts
immediately with iron and a precipitate is formed
30   which clogs the membrane.

        To summarize, the charge carrier comprises
sodium, potassium, lithium or ammonium ions, going
from the $-^{ve}$ side to the $+^{ve}$ side through the membran
during the discharge portion of a cycle. The ferric
35   ions in the $+^{ve}$ side are reduced to ferrous ions during

discharge, and the S^{2-} ions in the $-^{ve}$ side are oxidized to sulfur (solubilized as polysulfide ion during discharge). The total voltage for this process is 1.15 to 1.25 volts open circuit. With the

5      $+^{ve}$ side $Fe^{3+} + e^- \rightarrow Fe^{2+}$, providing 0.70 to 0.75 volts, and the

$-^{ve}$ side $S^{2-} \rightarrow S + 2e^-$, providing 0.45 to 0.50 volts

During charging, K^+ ions are transported across

10   the membrane from the $+^{ve}$ to the $-^{ve}$ side to balance the charge and transform K_2S_5 to K_2S. The sulfur which is present as a doubly charged polysulfide ion $S^{2-}.S_x$, (where x may be as high as 4), is reduced initially to $S^{2-}.S_{x-1}$, and eventually to S^{2-}. The Fe^{2+} is oxidized to

15   Fe^{3+} which goes into solution and is available to re-oxidize the S^{2-} ions back to sulfur during discharge.

Flow of the electrolytes on both sides of the membrane(s) is/are provided, preferably a re-

20   circulation rather than a once through flow in the majority of end uses. The recirculation of the electrolytes provides a chemical replenishment of the electrolytes which operates in the present invention in addition to the electrical restoration of the $+^{ve}$

25   and $-^{ve}$ electrolytes. These recirculating electrolytes are stored in independent containers where the quantity may be large enough for the specific requirements of a preferred embodiment. The circulation also allows the electrolytes to be

30   filtered, or otherwise reconstituted on a routine basis without taking the system off-line.

As the electrolyte in the $+^{ve}$ side is circulated, ferric ions in solution are absorbed at a surface of the $+^{ve}$ electrode and/or in a porous surface layer

35   thereof and replenished at such sites as discharge

reduces the ferric to ferrous ions. In addition, the
surface of the $+^{ve}$ electrode is preferably coated with
an active ingredient, preferably an activated carbon,
which augments the iron reaction kinetics. This
5   combination provides iron promptly for the discharge
requirements, and thus provides full power until
substantially fully discharged. During this discharge
the output voltage of the cell is nearly constant,
with little polarization loss.
10   The $-^{ve}$ side has a similar electrode which absorbs
the S^{2-} solution for subsequent discharge and enhances
performance similar to that described at the $+^{ve}$
electrode.

Mid electrodes (also defined as intermediate or
15   bipolar electrodes) combine the above such that a $+^{ve}$
electrode is provided on one surface, and a $-^{ve}$
electrode on another surface formed on the same
substrate.

Depending upon the membrane efficiency there may
20   be some diffusion of the iron ions into the $-^{ve}$
electrode side, resulting in a reagent loss on the $+^{ve}$
side, an electrolyte composition imbalance and a
coulombic loss. Restoration of electrolyte balance and
re-use of any iron sulfide precipitate is accomplished
25   during recharging via a separate system.

Alternative preferred embodiments substitute
sodium, lithium, or ammonium ions, or other
appropriate substitutes, for the potassium as the
charge carrier and in the sulfide solution.
30   Other objects, features and advantages will be
apparent from the following detailed description of
preferred embodiments thereof taken in conjunction
with the accompanying drawings in which:

FIGS. 1A and 1B are schematic views of the basic
35   compon nts of two cell types (A and B) us d according

to a preferred embodiment of the invention;

FIG. 1C is diagram of a cell array using the FIG. 1B type B cells;

FIG. 1D shows an encapsulation of an array of cells;

FIG. 1E shows a reclamation technique;

FIG. 2A is a block diagram of a full system using one or both types of the cells of FIG. 1A and FIG. 1B;

FIG. 2B shows a pH compensation cell on both sides;

FIG. 2C shows an alternative pH compensation cell in the $+^{ve}$ side utilizing a membrane;

FIG. 3 is a graph of certain cells during discharge.

FIGS. 4 and 5 are graphs of the charge/discharge characteristics of certain cells.

In the following description, reference is made to the specific system utilizing iron chloride, sodium chloride (as the charge carrier) and sodium sulfide. It will be understood, however, that other salts may be substituted for these salts, as appropriate.

Referring to the drawings, FIG. 1A shows a Type A cell 10 with a $+^{ve}$ electrode 12 and a $-^{ve}$ electrode 14. A cation membrane 16 is formed from a heterogeneous structure made by Sybron Chemical Co. called IONAC MC3470. In the above cell, the membrane 16 acts to separate the $+^{ve}$ and $-^{ve}$ sides of the cell 10 and is selected to minimize migration of iron from the $+^{ve}$ side to the $-^{ve}$ side and to minimize migration of S^{2-} ions from the $-^{ve}$ to the $+^{ve}$ side. An aqueous solution 22 of $FeCl_3$, $FeCl_2$ and $NaCl$ is provided in a chamber 22C formed between $+^{ve}$ electrode 12 and the membrane 16, and an aqueous solution 24 of Na_2S_x is provided in a chamber 24C formed between the $-^{ve}$ electrode 14 and the membrane 16.

When the cell and the electrolyte system feeding
it are in the charged state, a solution of ferric
chloride of up to 4.0 molar concentration exists in
the chamber 22C of the cell, and a solution of Na_2S at
2.5 molar concentration, exists in chamber 24C of the
cell.   Typically, each of chambers 22C, 24C has a
volume of about 200 cc. The cation membrane 16 allows
the passage of charge via the transport of Na^+ ions.

FIG. 1A illustrates a cell which though
rechargeable initially cannot be electrically
recharged indefinitely. In this embodiment, the
solutions should periodically be reconstituted
externally to the cell and replaced. The charge
carriers are the sodium ions (Na^+) which transfer
charge through the membrane 16. During discharge
(supplying power to an external load) the Na^+ ions are
moving from the $-^{ve}$ side to the $+^{ve}$ side through the
membrane. The ferric ions in the $+^{ve}$ side are being
reduced to ferrous ions, and the S^{2-} ions in the $-^{ve}$
side are being oxidized to sulfur (which is
solubilized by the sodium sulfide). Also during
discharge, the $-^{ve}$ ions are trying to move into the $-^{ve}$
side, but little Cl^- is lost since the membrane is a
cation exchange membrane.

The cation exchange membrane has to satisfy
certain conditions with respect to conductivity and
selectivity. It must freely transport Na^+ but exhibit
a low diffusion rate for Fe cations. However, most
cation exchange membranes, even the most selective,
have Fe diffusion rates of the order of 500 µg cm^{-2} h^{-1}
mol^{-1}. This effectively limits the charge/discharge
cycles in a single membrane cell as eventually some
iron will migrate across the membrane and react with
S^{2-} to form an insoluble precipitate in the membrane
surface layer.

The FIG. 1B, the Type B cell is electrically rechargeable. This embodiment has, in addition to the two chambers of the type A cell, an additional middle chamber 23C separated from the other two chambers enclosing the electrodes by two cation exchange membranes 16A and 16B. The center chamber has an NaCl or NaOH solution 23 circulating through it which does not change composition (an "idler" electrolyte). When charging, Na+ ions are transported from the $+^{ve}$ side, through the middle chamber 23C (both membranes) into the $-^{ve}$ side. However, should any Fe^{3+}, Fe^{2+} or S^{2-} ions be transferred to the middle chamber they can be filtered through filter 17 out of the solution. When NaOH is in the middle chamber, any Fe^{3+} or Fe^{2+} ions present in that chamber will be precipitated as the hydroxide. There may be a need for pH control in either or both of chambers 22C and 24C as described later.

Using the three chamber rechargeable cell illustrated in FIG. 1B means that any precipitation will occur in the middle chamber, and can be removed without interfering with the main electrolyte flow circuits.

When charging the three chamber cell, Na^{+} ions are transported across the cation membranes 16A and 16B from the $+^{ve}$ to the $-^{ve}$ side of the cell. The Na^{+} ions transform the Na_2S_5 to Na_2S and in the process S is reduced to S^{2-} ions. At the $+^{ve}$ side ferric ions are produced (via oxidation of the ferrous ions at the $+^{ve}$ electrode 12) and remain in solution 22 (posilyte).

After many cycles, the middle chamber will accumulate some amount of iron sulfide precipitates, e.g., FeS and Fe_2S_3. These materials will eventually need to be removed from the system, or recycled. A method for the recycling or reclamation of these

precipitates is shown in FIG. 1E. This method is a
totally self contained process (within the energy
system) and does not require the introduction of any
additional chemical reagents.

5   As the liquid 23 is circulated to the idler tank
chamber 25, it is passed through an ancillary
electrochemical cell 27 specifically designed for
reclamation. The $-^{ve}$ electrode 29 of this cell is
porous carbon which will collect the iron sulfide

10   precipitates as a filter in the stream of the liquid
23. The $+^{ve}$ electrode 30 is a lightly surfaced carbon
composite substrate.

          If the liquid 23 in the middle chamber 23C is an
NaCl or KCl solution, electrolysis will generate iron

15   within the porous carbon $-^{ve}$ electrode and H_2S at the
$+^{ve}$ electrode. The H_2S is vented from cell 27 as a gas
along line 31 back into the $-^{ve}$ electrolyte of the
power cell where it reacts with NaOH or KOH to form
Na_2S or K_2S, respectively, for reuse as the energy

20   storing reagents in the electrolyte. The reaction
within the reclamation cell is as follows:

          Eq. 3A $FeS + H_2O - Fe^\circ + H_2S + \frac{1}{2}O_2.$

25   The plated iron, Fe°, is later removed by the
direct action of Fe^{3+} ions in the positive side of the
power cell by hydraulically switching the reclamation
cell into the $+^{ve}$ electrolyte line.

          If the liquid 23 in the middle chamber 23C is an

30   NaOH or KOH solution, the reaction with the
reclamation cell is:

          Eq. 3B $FeS + 2NaOH - Fe^\circ + Na_2S + H_2O + \frac{1}{2}O_2.$

35   When providing power, th cell is discharging. In

both type A and type B cells similar reactions occur
at the two electrodes. At the $+^{ve}$ side electrode 12,
ferric ions are reduced to ferrous ions, Fe^{3+} to Fe^{2+},
and an electron is acquired from the external

5   circuit. At the $-^{ve}$ electrode 14 sulfide ions are
oxidized to molecular sulfur which is solubilized by
the sodium sulfide. The electrons produced at the $-^{ve}$
electrode form the current through a load. The
chemical reaction at the $+^{ve}$ electrode produces 0.7 to

10   0.75 volts (open circuit) and the chemical reaction at
the $-^{ve}$ electrode produces 0.45 volts (open circuit).
The combined reaction produces 1.15 to 1.20 volts per
cell (open circuit).

     FIG. 1C shows a cell array 20 of multiple cells

15   connected in electrical series and fluid parallel.
End electrodes 12E ($+^{ve}$) and 14E ($-^{ve}$) and multiple
mid-electrodes 13 (each one having a $+^{ve}$ electrode
portion 12A and $-^{ve}$ electrode portion 14A) are spaced
out from each other by membranes 16 and screen or mesh

20   spacers 22D, 24D in all the cell chambers 22C, 24C,
(portions of two of which 22D, 24D are shown by way of
example) to form end cells C_{E1} and C_{E2} and an array of
n# of mid cells C_M (typically 10-20; but note much
smaller and much higher numbers of cells can be

25   accommodated). The end electrodes 12E ($+^{ve}$) and 14E
($-^{ve}$) have internal conductors 12F and 14F (typically
copper screens) encapsulated therein and leading to
external terminals 12G, 14G which are connected to
external loads (e.g. to a motor M via a control

30   circuit CONT, the motor driving a vehicle) or to power
sources (e.g. a utility power grid when used as a load
levelling device).

     FIG. 1D shows the manner of encapsulating a cell
array such as that of FIG. 1C. A cell array 20 (such

35   as shown in FIG. 1C) is held between clamping blocks

CB and dipped at one edge into a shallow container having a bath of liquid epoxy resin (not shown) therein. The epoxy resin hardens to form a wall of the battery. Flow conduits such as manifold 22M with feed tubes 22N for the $FeCl_3$/NaCl solution feed are provided (a similar arrangement (not shown) being provided for the sodium sulfide solution feed). These flow conduits are simultaneously encapsulated with the electrode and membrane edges.

The cell array is rotated 90 degrees and the process repeated three times to form four long walls. Manifolds and tubes for electrolyte withdrawal are provided at the top face. Additional encapsulation can be provided at the backs of end electrodes 12E, 14E.

An alternative approach to encapsulation is to use a dissolvable or low melting point solid to fill the cell chambers 22C, 24C, and the manifolds and tubes of essentially all cells of battery 20. The battery is then dipped in its entirety into a deep epoxy resin bath. After the epoxy resin hardens, the battery is subjected to water or other solvent fed through its circulatory path to dissolve the solid, or is heated to melt the solid.

Another effective encapsulation approach is a plate and frame structure (not shown) which has enough short-term sealing integrity to permit a single pouring of encasing polymer (epoxy). The polymer provides the long-term sealing along all edges of the electrodes and membranes.

In either embodiment of encapsulation the goal is to safeguard against: (a) cell to cell leakage; (b) leakage between tubes and between manifolds; (c) leakage to the environment; and (d) to provide short lengths of narrow cross section tubes.

FIG. 2A shows a free flow system, a power generation/storage system utilizing one or more of the cells or cell array formats 20. Each cell 20 receives electrolyte through pumps 26 and 28 for the

5   $FeCl_3$/NaCl and Na_2S_5 solutions (22 and 24, respectively). The electrolytes 22 and 24 are stored in containers 32 and 34 large enough for the needs of a particular job. The tanks 32, 34 can be replaced with freshly charged electrolyte by substituting tanks

10 containing fresh electrolyte and/or refilling them from charged supply sources via lines 32R, 34R with corresponding lines (not shown) provided for draining spent (discharged) reagent.

15   Fabrication of electrodes

End electrodes differ from the mid electrodes because they must have a metallic conductor embedded within the structure running across the electrode

20 area. This is required because the resistivity of the substrate material from which they are formed is too high to allow adequate electrical conduction to an external electrical connector. For example a 25cm by 25cm square (10 inch by 10 inch square) of substrate

25 material of 0.25 cm (0.10 inch) thickness will have a resistance of about 10 ohms where a corresponding cell has an internal resistance of about 0.01 ohms. A sheet of copper of 0.025 cm (0.010 inch) thickness with approximately the same area embedded into the

30 electrode will reduce the effective resistance to about 100 micro ohms. The end electrodes are unipolar, whereas the mid-electrodes are bipolar. The conductor sheet is a thin screen structure embedded along the length of the end electrodes which make mechanically

35 good contact along the current path.

The process of making the bipolar mid-electrodes
is as follows. Substrates are formed of graphite
flakes mixed with a plastic binder or other suitable
binder, generally in a 1:1 weight ratio of such
5   components. The mixture is freed from moisture by
heating and/or desiccation methods, formed as sheets
and hot pressed at temperatures and pressures
appropriate to the materials used.

Then the substrates are coated on both the $-^{ve}$ and
10      $+^{ve}$ surfaces with activated carbon particles by placing
a sprinkling of such particles on mold plate surfaces
and hot pressing the substrates to complete sealing of
all voids in the substrate and to embed the particles
in its surfaces. Suitable types of activated carbon
15   for use in surfacing the electrodes are G212 of North
America Carbon Co., UU of Barnebey-Cheney Co., GAC of
Calgon Carbon Co., or PCB of Calgon Carbon Co.

After each pressing step, the press mold and its
contents are cooled under pressure by using a water
20   cooled heat exchanger to safeguard against bowing or
warping and also to ensure a compact, non-porous
structure.

End electrodes are prepared by making substrates
by mixing graphite flakes and a plastic binder
25   together, in the same general manner as described for
the process of making bipolar mid-electrodes.

These substrates are then formed into a sandwich
with a conductive screen, e.g. a copper screen, placed
therebetween. This assembly is hot pressed to form the
30   end electrode substrate and cooled under pressure to
minimize warping.

One surface of this substrate is then surfaced
with activated carbon or silic n dioxide particles, or
a mixture of silicon dioxide / activated carbon
35   particles, depending on whether a $-^{ve}$ electrode or a

+^{ve} electrode is being formed. This is effected by
placing a sprinkling of the required particles
(activated carbon or silicon dioxide) on the electrode
surface and hot pressing to embed the particles in the
5   surface thereof. After each pressing step the press
mold and its contents are cooled, for example using a
water-cooled heat exchanger to safeguard against
bowing or warping.

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Membranes

The preferred cation exchange membrane for use in
15   the present invention is a heterogeneous structure
made by Sybron Chemical Co. called IONAC MC3470 or
NAFION made by Du Pont de Nemours. IONAC is a cation
exchange membrane containing sulfonated resins as the
functional materials bonded together with Kynar. The
20   material is bonded to a fibrous support sheet of glass
cloth or polymer fiber. The specifications for this
membrane are: 0.040cm (0.016 inches) thick, 96%
permselectivity and 5 ohms/square cm in 1 N NaCl.

25   ## Compensation for migration

Because water is transferred across the membrane
by osmosis or electro-osmosis, it becomes necessary to
correct for this happening. This is accomplished by
30   reverse osmosis or by evaporation of water from the
appropriate electrolyte.

Power Enhancement

35   The surfaces of the electrodes are coated with a

porous activated carbon which acts to absorb the iron
solutions in the $+^{ve}$ side and to absorb the $S2^-$
solution in the $-^{ve}$ side. The large surface areas
enhance the availability of the iron and sulfur during
5   discharge. This enhancement provides better
performance by maintaining the output voltage and
power even when the cell is near complete discharge.
Polarization losses are low.

10   pH Compensation

In the $+^{ve}$ side of a cell the pH tends to rise
(become more basic) as time progresses. This is due to
the diffusion of H^+ ions from the chloride solution in
15   the $+^{ve}$ side to the $-^{ve}$ side, and in the $+^{ve}$ side the
$FeCl_2$ and $FeCl_3$ salts in water mix with oxygen from the
air forming iron oxides which eventually precipitate
out of solution. To counter this the pH of the
electrolyte in the $+^{ve}$ side should be kept below 4.
20   FIG. 2B shows a pH control system in which pH
control of both the $+^{ve}$ side and the $-^{ve}$ side of the
cell 10 is effected. It will be understood that pH
control will be required in some circumstances in one
side of the cell 10 only, and this is within the scope
25   of the invention.
Referring to the drawing, a pH control cell 50 is
positioned in the flow path of the electrolyte 22 from
the $+^{ve}$ chamber 22C of cell 10. A DC current is passed
from the $+^{ve}$ electrode 52 to the $-^{ve}$ electrode 54 of
30   the cell 50 at a voltage greater than 1.6 volts (in
order to overcome the open circuit voltage of the pH
control cell). The $+^{ve}$ electrode 52 has an activated
carbon surface 56 which absorbs the electrolyte
solution 22 and catalyses the formation of HCl and
35   HClO. At the $-^{ve}$ electrode 54 of the cell 50, iron is

produced which is dissolved by the ferric ions in the
electrolyte 22 to form ferrous ions.

A pH control cell 80 is positioned in the flow
path of the electrolyte 24 from the $-^{ve}$ chamber 24C of

5   the cell 10. The $-^{ve}$ side of cell 80 has a "starved"
cathode 86. A DC current is passed from the $+^{ve}$
electrode 82 to the $-^{ve}$ electrode 86, electrolyzing
water to produce H_2 gas at the cathode 86, with the OH^-
ions also produced raising the pH of the electrolyte

10   solution and thus compensating for the migration of
OH^- ions from the $-^{ve}$ side to the $+^{ve}$ side of cell 10.
The cathode 86 of cell 80 is "starved" to maximize the
OH^- ion production and to minimize the production of
sodium sulfide. The starving of the cathode 86 is

15   accomplished by surfacing the cathode with a thick
porous layer 88 which reduces the availability of the
sodium polysulfides at the $-^{ve}$ electrode surface, thus
promoting the electrolysis of water. A preferred
porous surfacing for the cathode 86 is an unwoven

20   polypropylene cloth, such as Webril cloth made by the
Kendall Co.

At the $+^{ve}$ electrode of the pH control cell 80,
the following reaction occurs:

25   <u>Eq. 4A</u> $S + Na_2S_x \rightarrow Na_2S_{x+1}$

At the $-^{ve}$ electrode of the pH control cell 80,
the following reaction occurs:

30   <u>Eq. 4B</u> $H_2O + e^- \rightarrow OH^- + 1/2H_2$
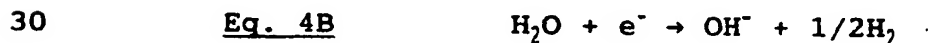
The H_2 gas may be vented from the tank 34 by
means of a vent 85.

The pH control cell 80 may, if desired, employ a

35   membrane in order to divide the cell into a $+^{ve}$ chamber

and a -^{ve} chamber. In such an embodiment the H_2 gas
product may be vented directly from the -^{ve} chamber of
the cell .

FIG. 2C shows a more complicated pH control cell
5   60 designed with two fluid chambers 72, 74 separated
by a cation exchange membrane 58. This cation exchange
membrane 58 permits only H^+ ions to transfer from the
+^{ve} to the -^{ve} side of the pH control cell 60. The cell
60 has a -^{ve} electrode 76 and a +^{ve} electrode 68. The
10   electrode +^{ve} 68 is starved of Cl^- ions by limiting the
flow 66 of the electrolyte 22 to the anode surface by
placing a diffusion limiting layer of a porous non-
conductive material 67, such as fluorocarbon particles
or silicon dioxide particles, on the anode surface. A
15   DC current is passed through the cell from the +^{ve}
electrode 68 to the -^{ve} electrode 76. At the +^{ve}
electrode 68 the electrolysis of water occurs forming
oxygen gas at the electrode 68 and hydrogen ions in
solution which are transported across the membrane 58
20   into the chamber 74 through which electrolyte stream
64 flows. These H^+ ions lower the pH of the
electrolyte 22. Some chlorine is also produced at the
+^{ve} electrode, but it reacts with the ferrous ions in
solution. The oxygen gas is vented into the main flow
25   path 70 of the electrolyte to the chamber 22C of cell
10.

At the +^{ve} side of the pH control cell 60, the
following reaction occurs:
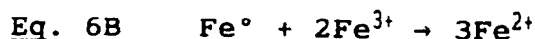
30        $$\underline{Eq.\ 5} \qquad H_2O \rightarrow 2H^+ + 1/2O_2 + 2e^-$$

At the -^{ve} electrode of the pH control cell 60,
iron is deposited on the -^{ve} electrode 76, but the
iron is dissolved by the ferric ions flowing through
35   the chamber 74.

At the $-^{ve}$ side of the pH control cell 60, the following reaction occurs, in two steps:

$$\underline{Eq.\ 6A}\qquad Fe^{2+} + 2e^- \rightarrow Fe^\circ$$

5

$$\underline{Eq.\ 6B}\qquad Fe^\circ + 2Fe^{3+} \rightarrow 3Fe^{2+}$$
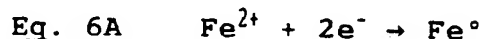
Specific embodiments

The present invention will be further described
10   with reference to the following non-limiting Examples.
Examples 1 and 2 are comparative Examples carried out
in cells in which no ionic salt is included in the
electrolyte circulating in the $+^{ve}$ chamber during
energy storage. In these comparative Examples the
15   cells were conducted as primary devices, i.e.
discharge only modes.

EXAMPLE 1

20   ## Fabrication of end electrodes

Two substrates were prepared by mixing graphite
flakes (#4012 graphite flakes of Asbury Carbon Co.)
with a polyvinylidene fluoride, PVDF, binder
25   (Penwalt's #461) in a 1:1 weight ratio. The mixture
was heated to remove moisture, formed into sheets and
hot pressed at a temperature of 177^0C (350°F) and a
pressure of 1723 kPa (250 psi) for 10 minutes, and
then cooled at the same pressure between water cooled
30   platens.

A stack was then formed, from bottom to top, of
an aluminum base plate, Teflon sheet, substrate, a
copper screen (0.025 cm. thick), the other substrate,
a Teflon sheet, high temperature rubber sheet, and
35   finally another aluminum base plate. The assembly was

then pressed at 1034 kPa (150 psi) at 177^{0}C (350°F)
for 10 minutes, and then cooled at the same pressure
between water-cooled platens.

5   The substrate to be surfaced had its edges
covered with tape and was then placed on an aluminum
base plate covered with a Teflon sheet, and a mixture
of 80% graphite and 20% Kynar sprinkled over the
surface. The surface of the substrate was then
sprinkled with a layer of activated carbon particles
10   (G212 of North American Carbon Co., or UU of Barnebey-
Cheney Co.).

A high temperature rubber sheet was placed on top
of the surfaced substrate, followed by a Teflon sheet
and an aluminum base plate. The structure was then
15   pressed at 517 kPa (75 psi) at 177^{0}C (350°F) for 10
minutes, and then cooled at the same pressure between
water-cooled platens.

The tape was then removed from the edges of the
surfaced side and a rubber "picture" frame placed on
20   top of the cleared border. The electrode was then
placed with the surfaced side uppermost onto an
aluminum base plate covered with a Teflon sheet and
the top surface of the structure covered with a Teflon
sheet and an aluminum base plate. The edges of the
25   assembly were pressed at 2413 kPa (350 psi) at 177^{0}C
(350°F) for 210 minutes,and then cooled at the same
pressure between water-cooled platens. This step
sealed the substrate sheets along the edges in order
to ensure that the copper screen was totally
30   encapsulated to prevent corrosion by the electrolyte.

Cell fabrication

A sealed single cell was made by placing a +^{ve}
35   electrode and a -^{ve} electrode together with an IONAC

MC3470 membrane therebetween. The four edges of the
cell were cast with an epoxy resin to encapsulate the
cell and ports formed to allow the electrolytes to be
supplied to and to be removed from the cell.

5   The construction of the cell ensures that the
copper screens and the wires attached, which make
electrical contacts to the cell, do not contact the
electrolyte.

10   <u>Cell Performance</u>

        The above described cell was used, with UU carbon
surfaced electrodes, spaced apart 0.50 inch, with the
space between the electrode surface and membrane on
15   each side being filled with G-212 porous carbon. The
active area of the cell was 129 sq. cm (20 sq. in.)
The electrolytes were:

Positive side .... 100 cc of 3 molar solution
                                   of $FeCl_3$
20   Negative side .... 100 cc of 2 molar solution
                                   of Na_2S
Cell resistance .... 0.2 ohms

        Both solutions were in the charged state
25   initially, and the cell was setup to be discharged
only.

        The maximum coulombic capacity of the cell
assuming that the reaction to the pentasulfide shown
30   below

<u>Eq.7</u> $8 \ FeCl_3 + 5 \ Na_2S \rightarrow 8 \ FeCl_2 + 8 \ NaCl + Na_2S_5$
goes to completion was:

        +ve side ...... 7.8 AH
        -ve sid ...... 9.6 AH
35   The capacity was limited, in these examples, by

the amount of $FeCl_3$ in solution in the positive side.

Four discharges were conducted, with the electrolyte being replaced after each discharge. Electrolyte replacement was accomplished by draining the cell compartments and refilling the compartments with fresh solutions three times in order to flush out the "spent" reagents within the surface pores of the porous G-212 carbon.

Table 1 gives the data obtained from these experiments.

Table 1

Discharge Data at The 2.0 Ampere Rate

Cycle #	AH Output	% of Reagent Fe^{3+} Utilization
1	5.5	71
2	5.0	64
3	5.2	67
4	4.8	62

EXAMPLE 2.

A cell was constructed in the manner as described in Example 1 except that the electrode-to-electrode spacing was 1.00 cm (0.40 inch). Even though the cell had static electrolytes (non-circulating) the solutions were stirred or agitated periodically to ensure adequate mixing and physical availability of ionic species at the electrode surfaces. The active area of the cell was 129 sq. cm. (20 sq. in.) with excess cell volume to accommodate additional

electrolyte.

The electrolytes were:

Positive side .... 200 cc of 3 molar solution
                               of $FeCl_3$

Negative side .... 200 cc of 2 molar solution
                               of Na_2S

Cell resistance .... 0.08 ohms

Both solutions were in the charged state initially, and the cell was setup to be discharged only.

The maximum coulombic capacity of the cell, assuming that the reaction to the pentasulfide shown in Eq. 7 goes to completion was:

$+^{ve}$ side ...... 15.6 AH

$-^{ve}$ side ...... 19.2 AH

The capacity was limited, in these examples by the amount of $FeCl_3$ in solution in the positive side.

Two discharges were conducted, with the electrolyte being replaced after each discharge. The first discharge was at a 2 amp rate, and the second at a 4 amp rate. The discharge was quite flat to over 90% depth of discharge. Charge output was approximately 9 AH at useful voltages.

Figure 3 is the discharge curve which is typical of the shape of the discharge curve for non-circulating electrolytes with adequate agitation or stirring. At various times during the discharging attempts were made to recharge the cell by connecting the $+^{ve}$ and $-^{ve}$ electrodes of the cell to the $+^{ve}$ and $-^{ve}$ terminals, respectively, of a DC power supply. Within 10 to 20 seconds at less than 1 amp initial current, the cell resistance rose from its 0.2 ohms to over 100 ohms, and current diminished to less than 10 ma. Cell resistance continued to rise as long as the "charging" power supply was connected to the terminals.

Upon removal of the charging circuit and
replacing the electrical load, the cell resistance
decreased to its normal 0.2 ohm value, and discharging
proceeded as usual. There were no observable
5   remaining effects within the membrane as a result of
the attempts to recharge electrically.

Since the available sodium ion concentration in
the $+^{ve}$ side is low, Fe^{3+} ions will tend to be the
predominant charge carriers during "recharge".
10   However, since substantially no Fe^{3+} ions are
transported across the membrane, the cation exchange
membrane is rendered essentially non-conductive in the
absence of charge carrying ions.

15

EXAMPLE 3

Cell tests in the previous two examples were
conducted as primary devices, e.g. only discharge
20   modes. These cells are essentially non-rechargeable
devices because of the necessary limitations imposed
by the membrane resistance to Fe^{3+} transport and by the
need to keep the two electrolytes apart. Only sodium
ions can be allowed to migrate across the membrane
25   during both charge and discharge with the Fe^{3+}/S^{2-}
couple.

In order to recharge this system electrically an
ionic salt needs to be present in the $+^{ve}$ chamber
during recharging and, furthermore, a configuration
30   with more than two chambers is preferable.

A cell was assembled to characterize a
rechargeable version of the above couple. The cell
had static electrolytes (non-circulating) and three
compartments. The $+^{ve}$ compartment contained the
35   oxidizing agent, $FeCl_3$, and NaCl in aqueous solution

and the $+^{ve}$ electrode. The $-^{ve}$ compartment contained
the reducing agent, Na_2S, in aqueous solution and the
$-^{ve}$ electrode. A middle compartment was an isolation
chamber or buffer compartment. It contained a 2 molar
5 solution of NaCl. Each of the three compartments was
separated by a cation membrane. The physical
parameters of the cell were as follows:

Single cell consisting of two identical end
electrodes and two cation exchange membranes.

10 Membranes .... SYBRON Cation membranes,

Electrodes .... UU carbon surfaced
substrates, prepared as described in Example 1

Compartment spacing for electrolytes..... 1.25 cm

(0.50 inch)

15 Active area .... 129 sq. cm

(20 sq. in).

Electrolytes were:

Positive side .... 200 cc of 3 molar solution of $FeCl_3$
and 1.5 molar solution of NaCl

20 Negative side .... 200 cc of 2 molar solution of Na_2S

Middle compartment ..... 200 cc of 2 molar NaCl

Cell resistance .... 0.1 ohms

Both solutions were in the charged state
initially.

25   The maximum coulombic capacity of the cell,
assuming that the reaction to the pentasulfide shown
in Eq. 7 goes to completion was:

$+^{ve}$ side ...... 15.6 AH

-ve) side ...... 17.9 AH

30   The capacity was limited, in these examples by
the amount of $FeCl_3$ in solution in the positive side.

Three partial cycles were run with the same
electrolyte.

Table 2 gives the data obtained from these
35 experiments.

Table 2

Discharge Data at The 2.0 Ampere Rate

Cycle #	AH Output	AH Input	AH Efficiency	% of Reagent Fe^{3+} Utilization
1	10	12	83	64
2	12	14	86	77
3	9	11	82	58

Examination of the middle chamber electrolyte after the three discharges showed virtually no discoloration from the initial colorless and clear appearance. Only a very slight cloudiness was detected which might indicate some presence of free sulfur or other insoluble compounds such as iron sulfide compounds.

EXAMPLE 4

A cell was constructed in the manner as described in Example 1 with a UU carbon surfaced -^{ve} electrode and a GAC carbon surfaced +^{ve} electrode. The electrodes were separated by a Nafion 117 membrane, the electrode spacing being 0.50cm. The active area of the cell was 155cm^2.

The electrolytes were:

Positive side .... 150cc of solution of 3 molar FeCl$_3$ and 150cc of molar NaCl

Negative side .... 300cc of 1.25 molar solution of Na$_2$S$_5$

Cell resistance .... 78 milliohms

Th electrolytes were recirculated through the respective compartments of the cell.

Both electrolytes were in the charged state initially. The cell was discharged and charged over
5   two cycles at 3 amps. The results are given in Figure 4. It can be seen from these results that the charging potentials indicate a very large increase in resistance.

10   EXAMPLE 5

A cell was constructed in the manner as described in Example 4 with the compartments separated by Nafion 117 membranes. The electrolytes circulating in the $+^{ve}$
15   and $-^{ve}$ compartments were as described in Example 4. The middle chamber was a buffer chamber or isolation chamber through which 350cc of a 2 molar solution of NaCl was circulated.

The spacings between the cell components were
20   0.25cm from $-^{ve}$ electrode to membrane. 0.62cm between the two membranes, and 0.25cm from $+^{ve}$ electrode to membrane. The active area of the cell was 155cm^2.

The cell resistance was 106 milliohms.

Both electrolytes were in the charged state
25   initially. The cell was discharged and charged over three cycles at 3 amps. The results are given in Figure 5. It can be seen from these results that the charging potentials indicate a very large increase in resistance. The resistance of the cell is, however,
30   lower than that of the single membrane cell used in Example 4.

35

CLAIMS

1.   An electrochemical process for energy storage and power delivery comprising the steps of:

(a)   maintaining circulating electrolyte flows in a single cell or in an array of repeating cell structures, each cell with a chamber ($+^{ve}$ chamber) containing a $+^{ve}$ electrode and a chamber ($-^{ve}$ chamber) containing a $-^{ve}$ electrode, said chambers being separated one from another by a cation exchange membrane, wherein the electrolyte circulating in the $+^{ve}$ chamber during power delivery contains Fe^{3+} ions and during energy storage contains Fe^{2+}, wherein the electrolyte circulating in the $-^{ve}$ chamber during power delivery contains sulfide ions and during energy storage contains polysulfide ions and wherein the electrolyte circulating in the $+^{ve}$ chamber during energy storage additionally comprises a soluble, ionic salt, which is a sodium, potassium, lithium or ammonium salt, which acts as the charge carrier during energy storage, and

(b)   at least partially electrically restoring the electrolytes in said $+^{ve}$ chambers and $-^{ve}$ chambers by reversing the polarity on the $+^{ve}$ and $-^{ve}$ electrodes and providing sufficient voltage to drive the chemical reaction in the reverse direction.

2.   A process as claimed in claim 1 wherein the Fe^{3+} ions are provided in the electrolyte circulating in the $+^{ve}$ chamber as the chloride, bromide or iodide salt.

3.   A process as claimed in claim 1 or claim 2 wherein the ionic salt is a chloride, bromide or iodide.

4.   A process as claimed in claim 3 wherein the ionic
salt is sodium chloride or potassium chloride.

5.   A process as claimed in any one of the preceding
5   claims wherein the sulfide is sodium sulfide or
potassium sulfide.

6.   A process as claimed in any one of the preceding
claims wherein the electrolytes are chemically
10   replenished by circulating the electrolyte from each
chamber to storage means comprising a volume of
electrolyte greater than the cell volume for extended
delivery of power over a longer discharge cycle than
the cell volume alone would permit.
15

7.   A process as claimed in any one of the preceding
claims wherein the cell structures are subjected to
alternate electrochemical charge / discharge cycles.

20   8.   A process as claimed in any one of the preceding
claims which additionally comprises compensating for
the effect of changing pH in one or both chambers.

9   A process as claimed in claim 8 wherein the pH
25   compensation comprises the steps of flowing the
circulating electrolyte from the $+^{ve}$ chamber through a
pH control cell, driving a DC current through the said
pH control cell from a $+^{ve}$ electrode to a $-^{ve}$ electrode
thereof, thereby producing the H^+ ions and lowering
30   the pH of the electrolyte.

10.   A process as claimed in claim 8 wherein the pH
compensation comprises the steps of flowing the
circulating electrolyte from the $-^{ve}$ chamber through a
35   pH control cell, driving a DC current through the said

pH control cell from a +^{ve} electrode to a -^{ve} electrode
thereof, thereby producing OH$^-$ ions and raising the pH
of the electrolyte.

5   11.   A process as claimed in any one of the preceding
        claims wherein the +^{ve} and -^{ve} electrodes comprise
        conductive porous particles arranged to increase the
        available surface area of the electrodes and to
        increase the electrode surface wettability whereby the
10   surface resistance of the electrodes is substantially
        lowered.

        12.   A process as claimed in claim 11 wherein the
        conductive porous particles are activated carbon
15   particles.

20

25

30

35

FIG. 1A.

10

16

12

22C

24C

14

Na^+

$FeCl_2$
$FeCl_3$
$NaCl$

22

Na_2S_x

24

FIG. 1B.

20

16A

16B

12

14

Na^+

22C

23C

24C

$FeCl_3$
$FeCl_2$
$NaCl$

22

Na_2S_x

24

23

17

FILTER

NaCl
AND/OR
NaOH

FIG. 1C.

POWER SOURCE OR LOAD

CONTROLLER

FeCl₃
FeCl₂
NaCl

NaOH
NaCl

Na₂Sₓ

FIG. 1D.

CB

CB

FIG. 1E.

FIG. 2A.

NaCL
AND/OR
Na OH

FIG. 2B.

FIG. 2C.

FIG. 3.

CELL VOLTAGE

ELAPSED TIME - HOURS

-□- 2 AMP RATE   -◇- 4 AMP RATE
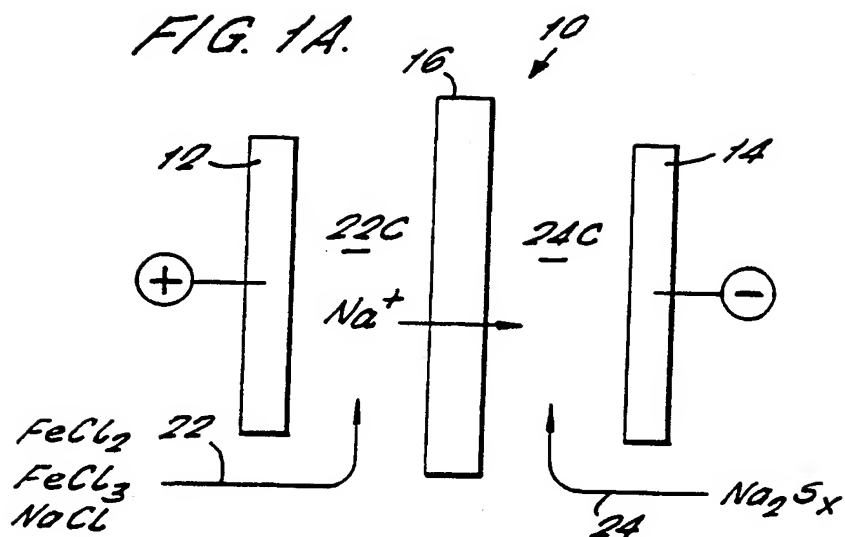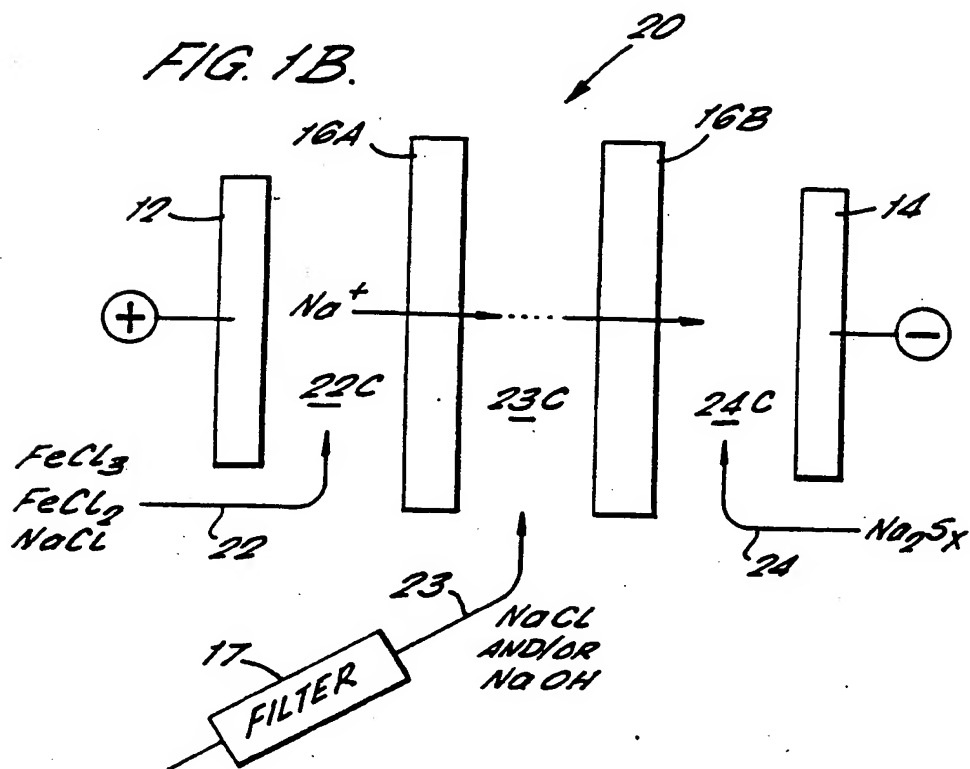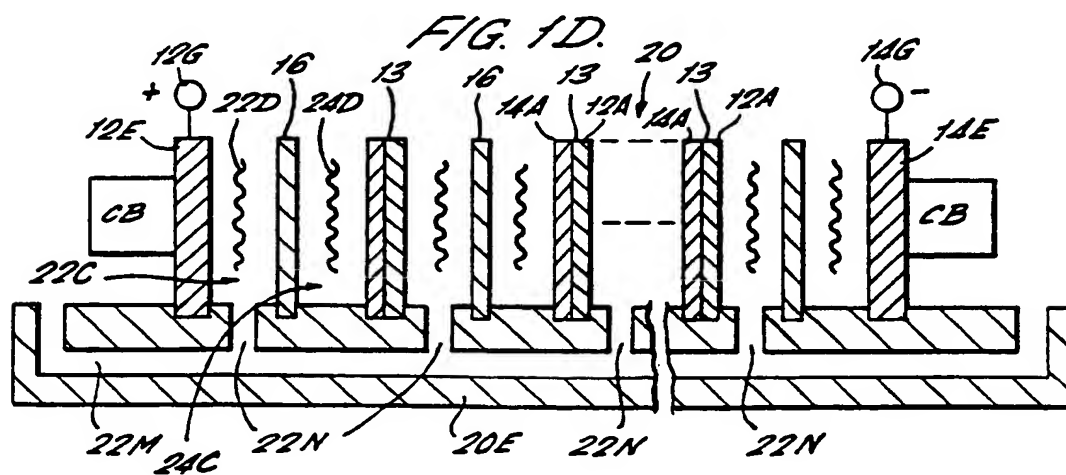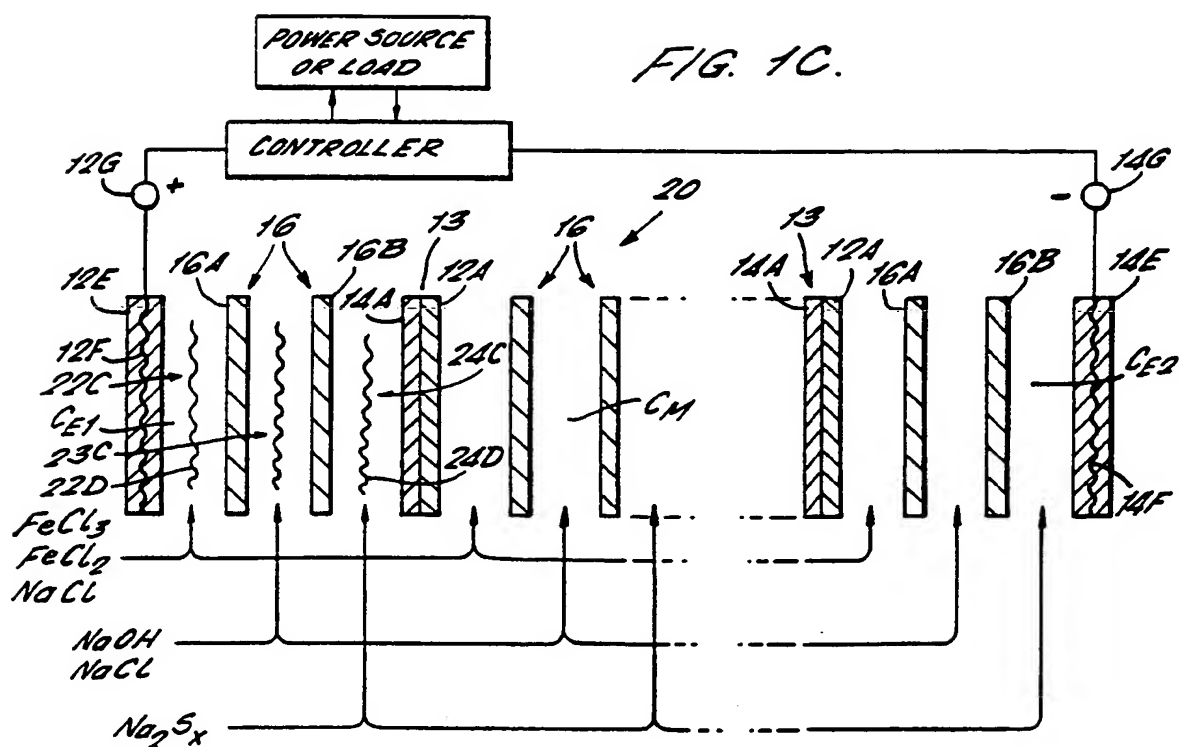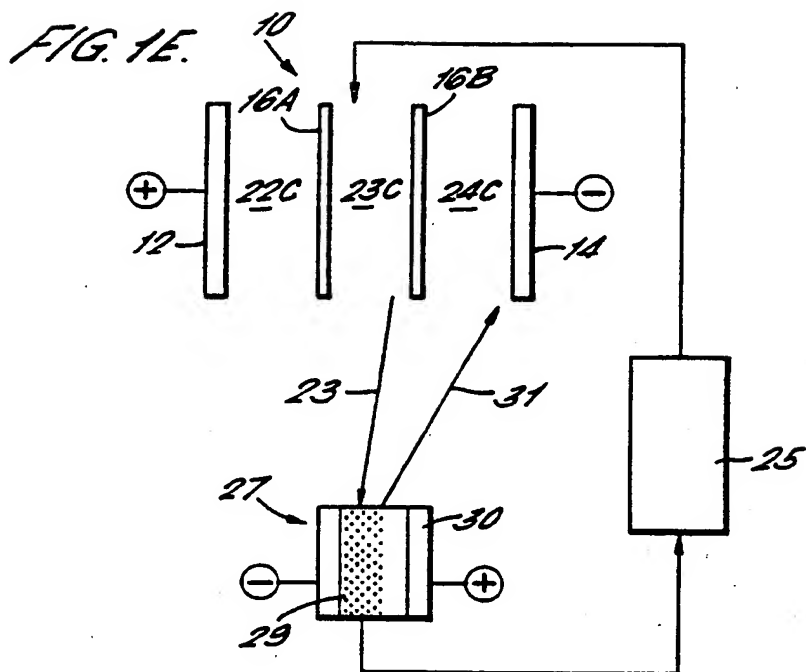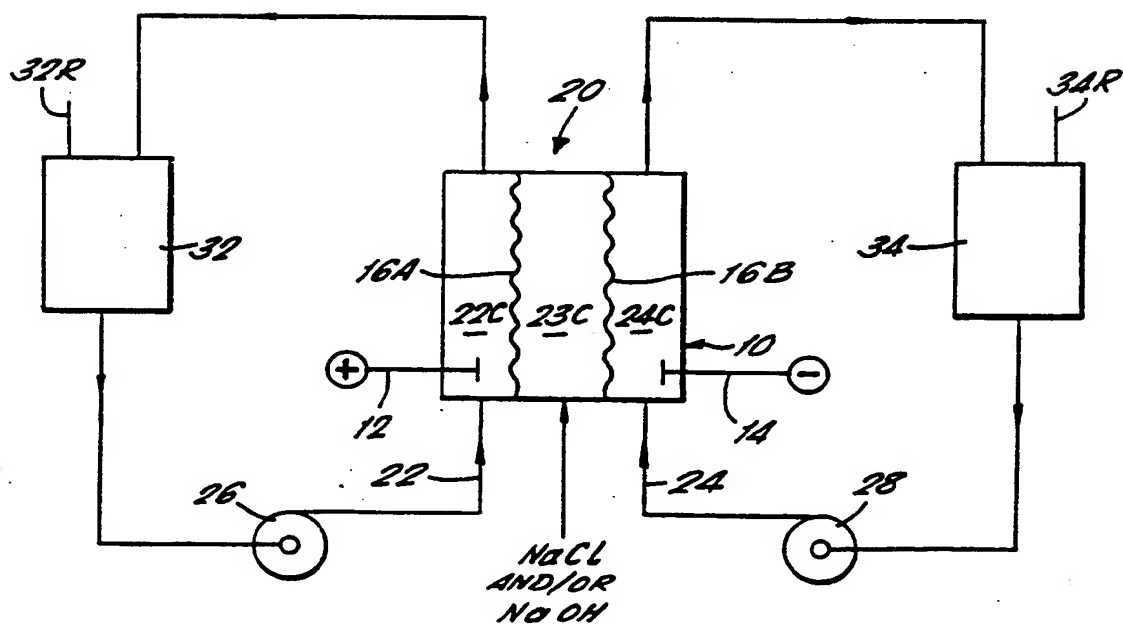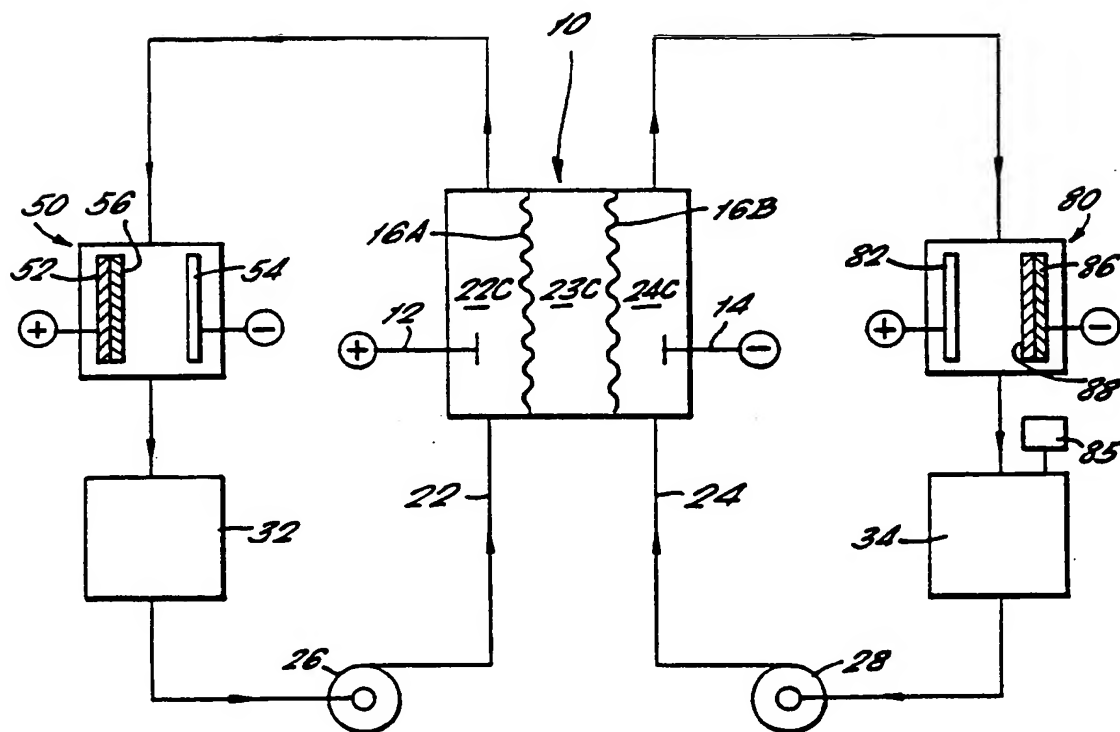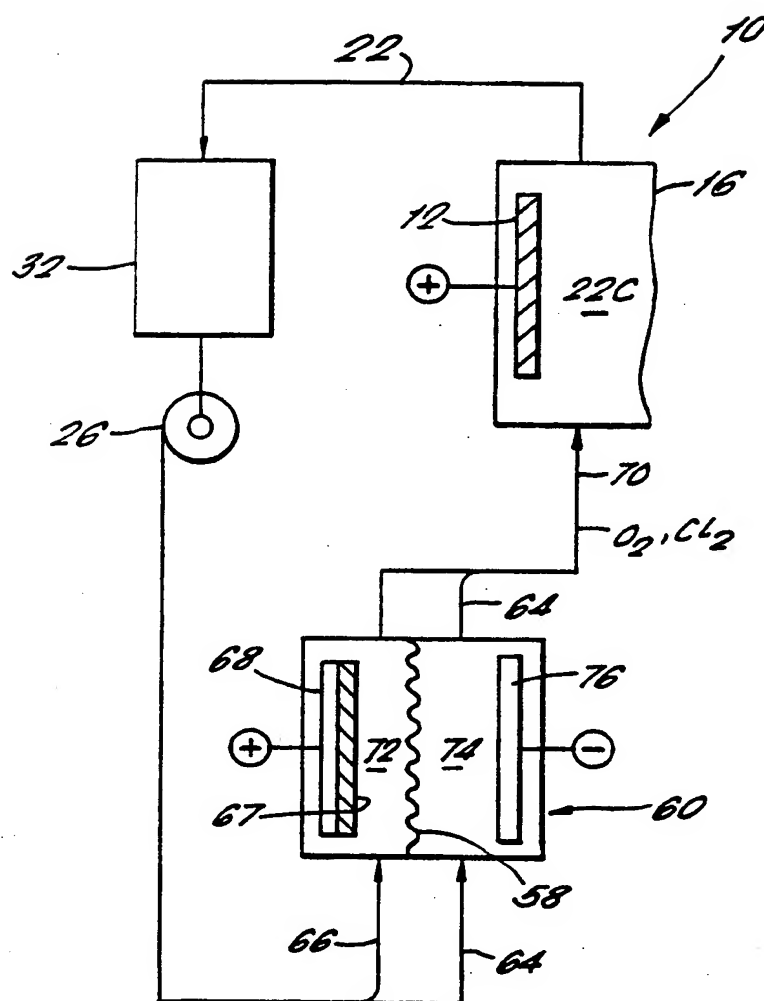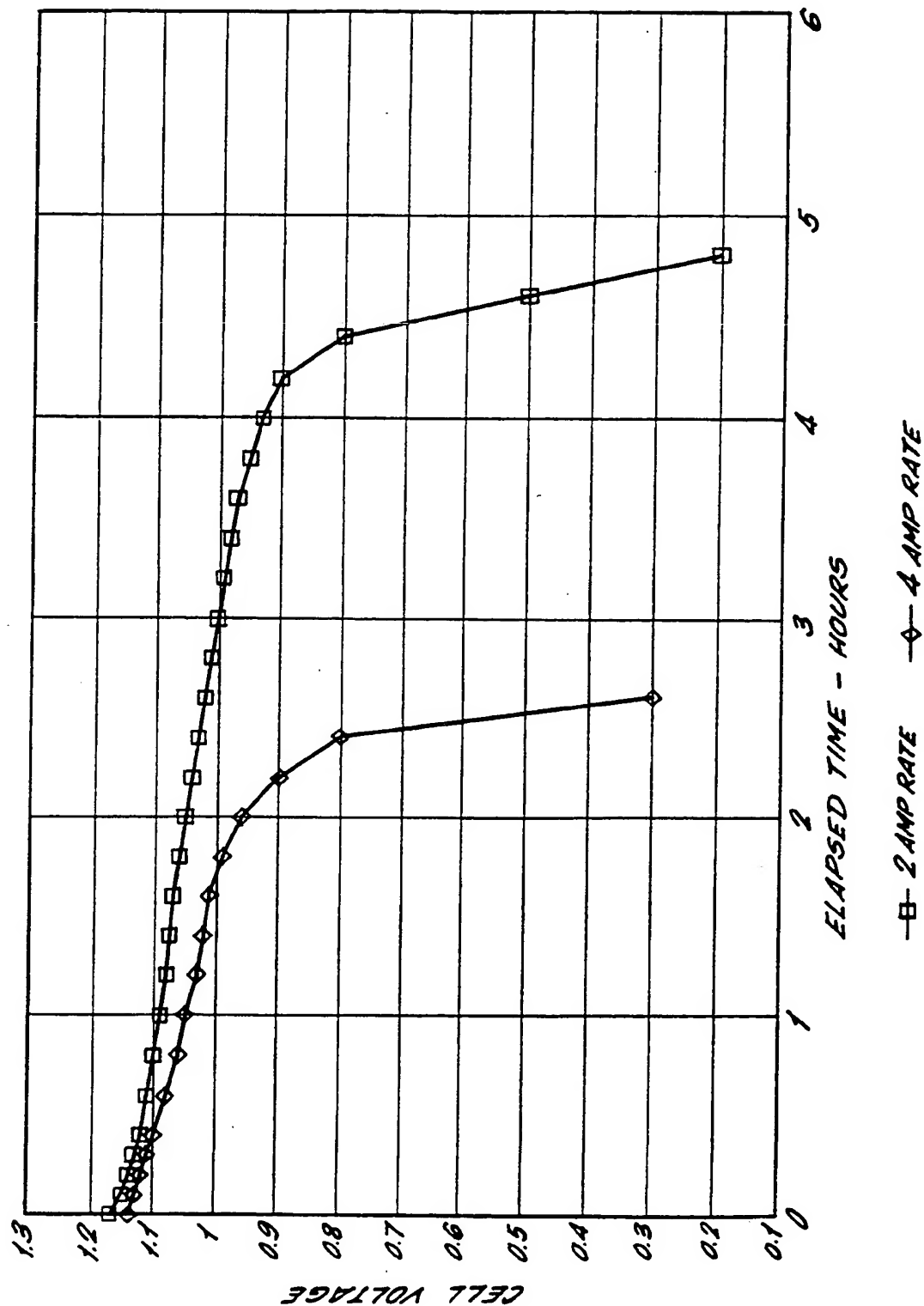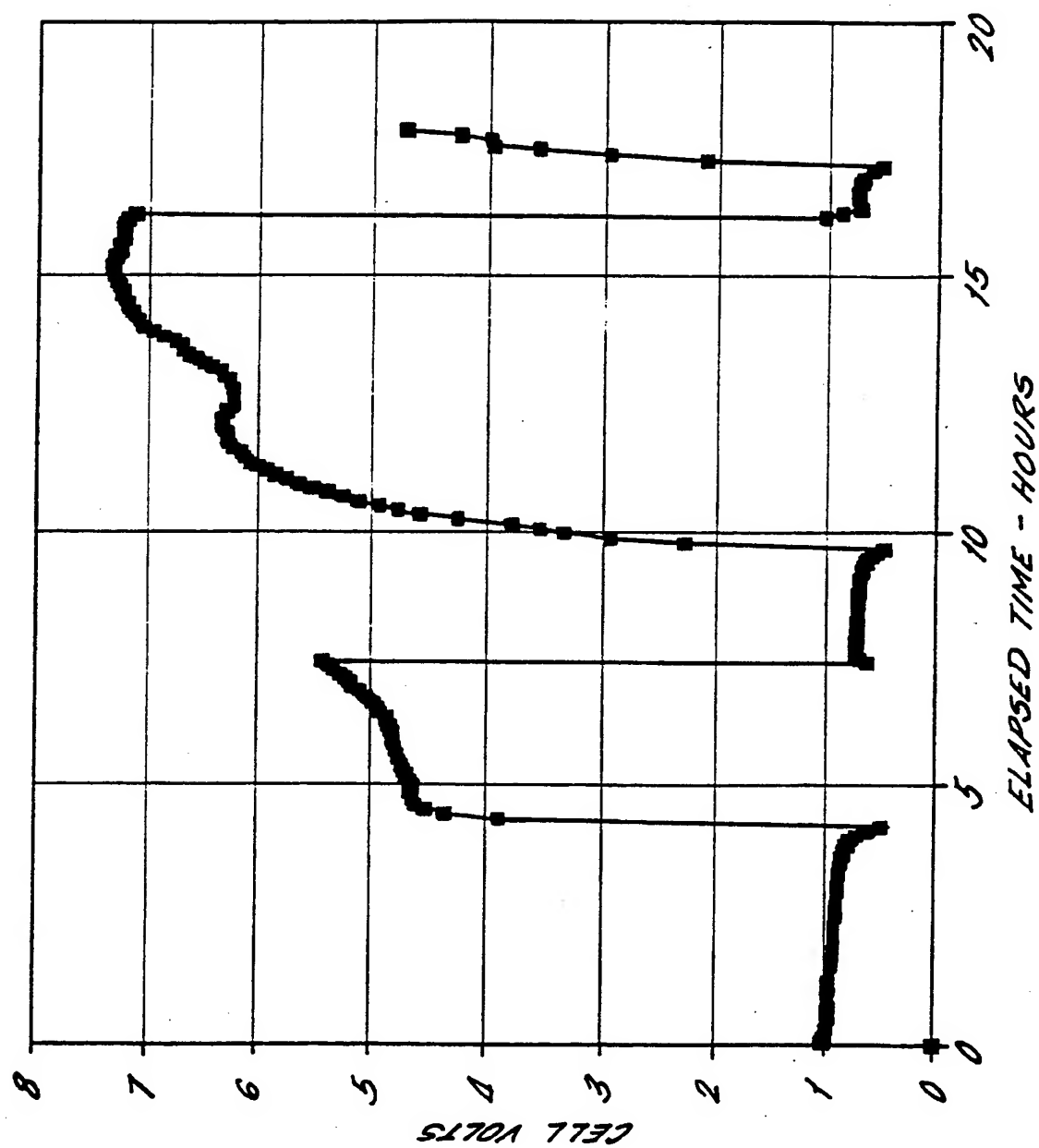
FIG.4.
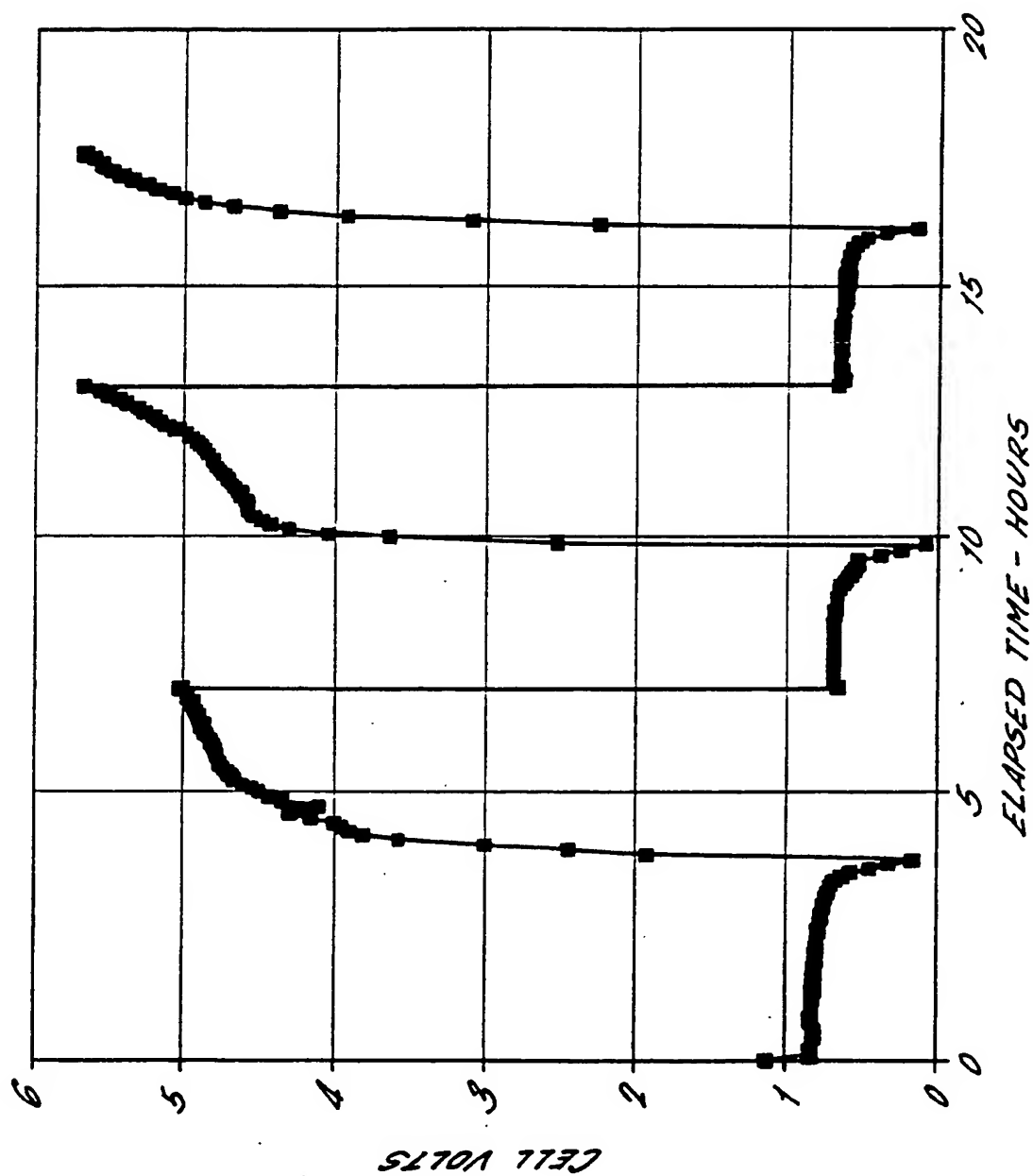
FIG.5.

International Application No

/GB 93/02109

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5   H01M8/18   H01M8/04   H01M8/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 · H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,3 920 474 (RALPH ZITO JR. ET AL) 18 November 1975 cited in the application see column 2, line 3 - line 31 see column 5, line 11 - column 6, line 9 see claims 1,2,4,5,9; example 6 ---	1,5,12, 13
A	US,A,4 485 154 (R. J. REMICK ET AL) 27 November 1984 cited in the application see column 2, line 36 - line 64; claims 1,2,5 see column 5, line 6 - line 15 ---	1,5,7
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
20 January 1994	27. 01. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	D'hondt, J

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 069 371 (RALPH ZITO) 17 January 1978 see column 4, line 20 – line 44 see column 8, line 43 – line 50; claims 2,12 see column 19, line 23 – line 42; figure 5 ---	8,9
A	PATENT ABSTRACTS OF JAPAN vol. 8, no. 13 (E-222)(1450) 20 January 1984 & JP,A,58 176 880 (KOGYO GIJUTSUIN) 17 October 1983 see abstract -----	6

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1

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3920474	18-11-75	NONE	
US-A-4485154	27-11-84	NONE	
US-A-4069371	17-01-78	NONE	